

Substitute Specification

TITLE OF THE INVENTION

Process for Producing Polybutadiene Rubber and Rubber
Composition

CROSS-REFERENCE TO RELATED APPLICATION

This application is a section 371 of International Application No. PCT/JP2005/023377, filed December 20, 2005, which was published in the Japanese language on May 26, 2006, under International Publication No. WO 2006/054808 A1 and the disclosure of which is incorporated herein by reference.

Technical Field

[0001]

The present invention relates to a process for producing a vinyl-cis-polybutadiene rubber and in particular, to a process for producing a vinyl-cis-polybutadiene rubber having excellent extrusion processability, tensile stress and flex crack growth resistance, which is suitable for automobile tire members, especially sidewalls, and to a rubber composition using the subject rubber.

Also, the invention relates to a rubber composition for sidewalls made of novel vinyl-cis-polybutadiene, which has a small die swell and excellent extrusion processability and which is capable of improving low fuel consumption with respect to a vulcanizate thereof.

Also, the invention relates to a silica compounded rubber composition suitable for tire cap treads, which has a small die swell and excellent extrusion processability while keeping excellent wet skid performance, exothermic characteristic and abrasion resistance as required for the performance of tires such as safety and economy.

Also, the invention relates to a passenger automobile tire using, as a cap tread rubber, a rubber composition having a small die swell and excellent extrusion processability while keeping a high elastic modulus.

Also, the invention relates to a rubber composition for internal members of tire such as tire coating rubbers inclusive of carcasses and belts, which has a small die swell, excellent extrusion processability and satisfactory adhesiveness to metals.

Also, the invention relates to a rubber composition for base treads and more specifically, to a rubber composition for base treads made of novel vinyl-cis-polybutadiene capable of making both internal exothermic characteristics of a tire and extrusion processability compatible with each other in a good balance.

Also, the invention relates to a high-hardness compounded rubber composition and more specifically, to a rubber composition suitable for beads and chafers of tire, which has improved dimensional stability (die swell is small) at the time

of extrusion processing or durability while keeping a high hardness.

Also, the invention relates to a rubber composition for large-sized vehicle tires using a rubber composition for a cap tread rubber, which has a small die swell and excellent extrusion processability while keeping high elasticity.

The rubber composition of the invention which is used in a tire can be further used for tire members such as tire sidewalls, cap treads, side reinforcing layers of run flat tire, carcasses, belts, chafers, base treads, beads, stiffners, and inner liners; industrial products such as rubber vibration insulators, hoses, belts, rubber rolls, rubber coolers, and shoe sole rubbers; and other composites, adhesives, plastic modifiers, and so on.

Background Art

[0002]

Polybutadiene has a so-called microstructure in which a binding segment formed by polymerization at the 1,4-positions (1,4-structure) and a binding segment formed by polymerization at the 1,2-positions (1,2-structure) are copresent in the molecular chain. The 1,4-structure is further classified into a cis-structure and a trans-structure. On the other hand, the 1,2-structure takes a structure containing a vinyl group as a side chain.

[0003]

Hitherto, a production process of a vinyl-cis-polybutadiene rubber composition has been carried out in an aromatic hydrocarbon-based solvent such as benzene, toluene, and xylene. When such a solvent is used, since the viscosity of a polymerization solution is high, there were problems in stirring, heat transfer, delivery, and so on, and excessive energy was required for recovering the solvent.

[0004]

As the foregoing production process, there is known a process in which 1,3-butadiene is subjected to cis-1,4-polymerization in the foregoing inert organic solvent by using a catalyst obtainable from water, a soluble cobalt compound and an organoaluminum chloride represented by the general formula, $\text{AlR}_n\text{X}_{3-n}$ (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group; X represents a halogen atom; and n represents a numeral of from 1.5 to 2) to produce BR, and 1,3-butadiene is then subjected to syndiotactic 1,2-polymerization (hereinafter abbreviated as "1,2-polymerization") in the presence of a catalyst obtainable from a soluble cobalt compound, an organoaluminum compound represented by the general formula, AlR_3 (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group or a cycloalkyl group) and carbon disulfide by adding or not adding 1,3-butadiene and/or the foregoing solvent to this polymerization system (see, for

example, JP-B-49-17666 (Patent Document 1) and JP-B-49-17667 (Patent Document 2)).

[0005]

Furthermore, for example, JP-B-62-171 (Patent Document 3), JP-B-63-36324 (Patent Document 4), JP-B-2-37927 (Patent Document 5), JP-B-2-38081 (Patent Document 6) and JP-B-3-63566 (Patent Document 7) describe a process in which the production is carried out by subjecting 1,3-butadiene to cis-1,4-polymerization in the presence or absence of carbon disulfide, or after the production, 1,3-butadiene and carbon disulfide are separated and recovered, thereby circulating 1,3-butadiene not substantially containing carbon disulfide or the foregoing inert organic solvent. In addition, JP-B-4-48815 (Patent Document 8) describes a rubber composition having excellent tensile stress and flex crack growth resistance, in which a compounded material thereof has a small die swell ratio and a vulcanizate thereof is suitable as a sidewall of tire.

[0006]

Furthermore, JP-A-2000-44633 (Patent Document 9) describes a process in which the production is carried out in an inert organic solvent containing, as the major component, a C4 fraction such as n-butane, cis-2-butene, trans-2-butene, and butene-1. It is described that in this process, 1,2-polybutadiene contained in the rubber composition is a short fiber crystal, and the distribution of the major axis length of the

short fiber crystal is such that 98 % or more of the fiber length is less than 0.6 μm and 70 % or more thereof is less than 0.2 μm . Also, it is described that in the resulting rubber composition, the moldability, tensile stress, tensile strength and flex crack growth resistance of a cis-1,4-polybutadiene rubber (hereinafter abbreviated as "BR") are improved.

[0007]

However, it is desired that not only the moldability is further enhanced, but also various characteristics are improved depending upon the utility. Furthermore, the foregoing vinyl-cis-polybutadiene rubber involved such a defect that it is inferior to usual high cis-polybutadiene with respect to exothermic characteristics and rebound resilience.

[0008]

Furthermore, in general, it is known that a proportion of the tire rolling resistance occupying in the running resistance which largely affects the fuel consumption of an automobile is large and that the affect due to an energy loss of sidewall rubber is relatively large. For that reason, rubbers having a low dissipation factor such as natural rubbers, isoprene rubbers, butadiene rubbers, and mixtures thereof have hitherto been used in the sidewall part. However, it is required that the rolling resistance of tire is further improved.

As a method for reducing the dissipation factor of the sidewall rubber, the use of carbon black having low reinforcing

properties or a reduction of the compounding amount of carbon black may be thought. However, there is encountered such a problem that the die swell at the time of extrusion processing becomes large, and therefore, it is difficult to make the thickness of the sidewall member thin or to realize an enhancement of uniformity of tire. For that reason, there is demanded a method for realizing low fuel consumption while keeping a small die swell with respect to an extrudate thereof.

[0009]

Furthermore, in general, with respect to the performance of automobile tire, there are required excellent wet skid properties as a braking characteristic and excellent rolling resistance ($\tan \delta$) or abrasion resistance as a fuel consumption characteristic. However, it is known that these characteristics are in an antinomy relation with each other. In recent years, though there has been made a proposal to compound silica having excellent wet skid properties, thereby highly balancing the foregoing characteristics, such is not satisfactory yet. It is known that though the silica compounding is excellent in the wet skid properties and fuel consumption properties, the abrasion resistance and processability are lowered. While the abrasion resistance is improved by the use of high cis-BR, there is some possibility that the wet skid properties are lowered, and therefore, improvements were demanded.

[0010]

Furthermore, in general, tires are required to have excellent drivability and durability and so on. In particular, from the standpoint of safety, the tires are required to have excellent wet skid resistance on a wet road surface. Moreover, on the basis of social requirements for realizing conservation of natural resources in recent years, tires having a low rolling resistance, namely tires with a low energy loss, are being researched and developed. While the energy loss of tire as consumed by free rotation varies depending upon the tire structure, etc., about a half of the whole energy is consumed in the tread part. Accordingly, if the energy loss of the tread rubber is reduced, a tire with a low energy loss at the time of rolling is obtained.

Then, it is attempted to modify the tread rubber such that the energy loss is low. However, such modification of the rubber tends to lower the wet skid properties. Since an improvement of the rolling resistance and an improvement of the wet skid properties generally contradict to each other, various designs for the improvements in the tire structure are attempted in order to make them compatible with each other. As one of the designs, there is enumerated a method for forming a tread into two layers consisting of a cap tread and a base tread. That is, this method is to form the tread into two layers of a cap tread with excellent wet skid properties and a base

tread with a low energy loss, thereby not only enhancing the wet skid properties of tire as a whole but also lowering the energy loss.

The rubber for cap tread is required to have a high elastic modulus and molding stability derived from the abrasion resistance and high-speed running properties in addition to the wet skid properties. As a method for obtaining a rubber with a high elastic modulus, various methods have hitherto been attempted. The method for compounding a large amount of carbon black is not preferable because unification of rubbers is poor in the processing step, an electrical power load increases at the time of kneading or extrusion, and ML of the compounded material becomes large, whereby difficulty is accompanied at the time of extrusion molding. The method for compounding a large amount of sulfur involves such defects that sulfur causes blooming and that the crack growth becomes fast due to an increase of the degree of crosslinking. With respect to the addition of a thermosetting resin, since the thermosetting resin is low in compatibility with usually used natural rubbers or diene-based rubbers, when a large amount of the thermosetting resin is compounded, satisfactory dispersion is hardly obtained. Furthermore, since this mixed compound is hard even in an unvulcanized state, the load may become large in kneading or extrusion, or the molding processability of tire may be deteriorated. In a method for merely blending and

compounding single fibers, since binding between short fibers and the rubber is insufficient, creep may become large, or fatigue life may be lowered.

[0011]

As the rubber for base tread, a rubber with low exothermic characteristics is required. Examples of rubbers with low exothermic characteristics include natural rubbers, isoprene rubbers, and cis-1,4-polybutadiene rubbers, and compounded materials of such a rubber with carbon black are used. In order to reveal low exothermic characteristics by other materials than rubbers, it may be thought to use carbon black having a large particle size and low reinforcing properties or to lower the compounding amount of carbon black. However, these methods involve such problems that the elastic modulus or fatigue resistance of rubber is lowered and that the die swell becomes large. Furthermore, there is a method for revealing low exothermic characteristics by compounding short fibers of nylon or vynylon, thereby making the rubber have a high elastic modulus. However, since these short fibers are insufficient in adhesion to rubbers, there is encountered a problem that the fatigue life is short.

On the other hand, when a cap/base system is employed in passenger automobile tires, at the time of co-extrusion of a cap tread and a base tread, there is caused a problem that an extrudate is warped because of a difference in die swell between

the both members. If the die swell of the base tread rubber is made small, this problem is liable to be solved. If a large amount of carbon black with high reinforcing properties is compounded, though the die swell become small, the heat generation becomes large. Thus, a method which is satisfied with the die swell and low heat generation at the same time is desired.

[0012]

Furthermore, in general, in radial tires, a steel cord is used in view of high-speed durability and high-speed drivability. In the case of using a steel cord, a very large strain is liable to be gathered in a rubber in the vicinity of the steel cord at the time of running of tire. Accordingly, the rubber for steel cord is required to have a high elastic modulus and excellent adhesiveness to metals. Even in radial tires or bias tires using an organic fiber cord, rubbers having a high elastic modulus are preferable as the rubber for cord from the viewpoint of durability.

As a method for obtaining a rubber with a high elastic modulus, various methods have hitherto been attempted. The method for compounding a large amount of carbon black is not preferable because unification of rubbers is poor in the processing step, an electrical power load increases at the time of kneading or extrusion, and ML of the compounded material becomes large, whereby difficulty is accompanied at the time

of extrusion molding. The method for compounding a large amount of sulfur involves such defects that sulfur causes blooming and that the crack growth becomes fast due to an increase of the degree of crosslinking. With respect to the addition of a thermosetting resin, since the thermosetting resin is low in compatibility with natural rubbers or diene-based rubbers as usually used as a cord coating rubber, dispersion failure likely occurs, and crack resistance is deteriorated. Furthermore, conventionally known tire cord coating rubber compositions are small in green strength. Thus, materials having a large green strength are required in view of molding processability.

[0013]

Furthermore, in general, as rubber members to be disposed in the surroundings of tire bead, high-hardness rubbers are used. Examples thereof include a rubber composition having an increased compounding amount of carbon black and a rubber composition having a novolak type phenol resin compounded therein (see JP-B-57-30856) and a rubber composition having short fibers and an olefin-based resin compounded therein (see JP-A-7-315014).

With respect to a method for obtaining a high-hardness rubber composition, it is general to increase carbon black or to compound a fiber, a resin, etc. However, in all of these methods, there may be the case where the heat generation at the

Thereafter, 150 mL of butadiene, 1.1 mmoles of water, 3.5 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing to 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, thereby obtaining vinyl-cis-polybutadiene having an HI of 40.5 % in a yield of 66 g. 58 g of this vinyl-cis-polybutadiene was dissolved in cyclohexane to prepare vinyl-cis-polybutadiene slurry.

[0109]

(B) Production of cis-polybutadiene solution:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 3.0 L and purged with a nitrogen gas, 2.0 L of cyclohexane was charged and dissolved in 136 g of cis-cis-polybutadiene (a trade name: UBEPOL-BR130B) manufactured by Ube Industries, Ltd. and having an ML viscosity of 29, thereby preparing a cyclohexane solution of cis-polybutadiene.

[0110]

Production of vinyl-cis-polybutadiene rubber of mixture of (A) and (B):

The foregoing cyclohexane solution of cis-polybutadiene having 136 g of cis-polybutadiene dissolved therein was charged in a stirrer-equipped stainless steel-made reaction tank

having an internal volume of 5.0 L and purged with a nitrogen gas, to which was then added the foregoing vinyl-cis-polybutadiene cyclohexane slurry containing 58 g of vinyl-cis-polybutadiene while stirring. After adding the slurry, the stirring was continued for one hour, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 194 g of a vinyl-cis-polybutadiene rubber of a mixture of (A) and (B). This polymer mixture had an ML of 60 and an HI of 12.1 %.

[0111]

(Example 2-2)

Vinyl-cis-polybutadiene was obtained in the same manner as in Example 2-1, except for using BR150L (manufactured by Ube Industries, Ltd.) as the cis-polybutadiene in (B). This polymer mixture had an ML of 68 and an HI of 11.9 %.

[0112]

(Example 2-3)

Vinyl-cis-polybutadiene was obtained in the same manner as in Example 2-1, except for using BR01 (manufactured by JSR Corporation) as the cis-polybutadiene in (B). This polymer mixture had an ML of 69 and an HI of 12.0 %.

[0113]

(Example 2-4)

Vinyl-cis-polybutadiene was obtained in the same manner as in Example 2-1, except for dissolving 10 g of polyisoprene (IR2200, manufactured by JSR Corporation) having been

reprecipitated and purified in 1.0 L of the polymerization solution before the 1,4-cis-polymerization in the production of vinyl-cis-polybutadiene in (A).

This polymer mixture had an ML of 62 and an HI of 12.1 %.

[0114]

(Comparative Example 2-1)

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5 L and purged with a nitrogen gas, 3.5 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 5.3 mmoles of water, 10.5 mmoles of diethylaluminum chloride, 1.8 mmoles of carbon disulfide, 40.0 mmoles of cyclooctadiene and 0.004 mmoles of cobalt octoate, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. Thereafter, 560 mL of butadiene, 4.5 mmoles of water, 13.4 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 60 °C for 20 minutes, thereby undergoing 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 350 g of a 1,4-cis-1,2-vinyl polymer. This VCR had an ML of 58 and an HI of 11.8 %.

[0115]

Each of the vinyl-cis-polybutadiene rubbers of the foregoing Examples and Comparative Example was subjected to primary compounding by adding thereto and kneading therewith carbon black, a process oil, zinc white, stearic acid and an antioxidant by using a plastomill and subsequently subjected to secondary compounding by the addition of a vulcanization accelerator and sulfur by using a roll according to a compounding table of Table 3, thereby preparing a compounded rubber. By using this compounded rubber, its die swell was measured. In addition, this compounded rubber was molded depending upon the desired physical properties and press vulcanized at 150 °C to obtain a vulcanizate, the physical properties of which were then measured. The measurement results of the respective physical properties are shown in Table 4 while taking the Comparative Example as "100".

[0116]

Table 3

	Compounding amount (parts by weight)
Vinyl-cis-polybutadiene	100
HAF carbon black	50
Process oil	10
Zinc white No. 1	5
Stearic acid	2
Antioxidant (Note 1)	1
Vulcanization accelerator (Note 2)	1
Sulfur	1.5

(Note 1) ANTAGE AS (a compound between amine and ketone)

(Note 2) NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0117]

Table 4

		Example 2-1	Example 2-2	Example 2-3	Example 2-4	Comparative Example 2-1
Component (A):						
Mooney viscosity of cis-polybutadiene		34	34	34	-	-
Viscosity in toluene solution of cis-polybutadiene		88	88	88	-	-
Mooney viscosity of polysoprene (IR)	H.I. (%)	-	-	-	90	-
		40.5	40.5	40.5	36.2	-
Component (B):						
Mooney viscosity						
Viscosity in toluene solution		29	43	44	29	-
Whole polymer (A + B):						
Mooney viscosity		30	105	150	30	-
IR (%)		60	68	69	62	58
H.I. (%)		-	-	-	5.0	-
		12.1	11.9	12.0	12.1	11.8
Physical properties of compounded material:						
Die swell		95	92	94	93	100
Physical properties of vulcanizate:						
Tensile elastic modulus M100		112	122	118	115	100
Rebound resilience		101	103	102	102	100
Flexometer test:						
Heat build-up ΔT		99	96	98	97	100
Permanent set		97	94	97	96	100

[0118]

(Example 3-1)

(A) Production of vinyl-cis-polybutadiene:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 1.5 L, 40 g of a cis-polybutadiene rubber (a trade name: UBEPOL-BR130B) manufactured by Ube Industries, Ltd. and having been reprecipitated purified was charged, and after purging with a nitrogen gas, 350 mL of cyclohexane was added for dissolution. To this solution, 150 mL of butadiene, 1.1 mmoles of water, 3.5 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing to 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto. Thereafter, the unreacted butadiene was removed by evaporation, thereby obtaining vinyl-cis-polybutadiene having an HI of 36.2 % in a yield of 63 g. 58 g of this vinyl-cis-polybutadiene was dissolved in cyclohexane to prepare vinyl-cis-polybutadiene slurry.

[0119]

(B) Production of cis-polybutadiene:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 1.5 L and purged with a nitrogen gas, 1.0 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by

weight) was charged, to which were then added 1.7 mmoles of water, 2.9 mmoles of diethylaluminum chloride, 20.0 mmoles of cyclooctadiene and 0.005 mmoles of cobalt octoate, and the mixture was stirred at 60 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, thereby obtaining 81 g of cis-polybutadiene having a Mooney viscosity of 29 and a viscosity in a toluene solution of 48. This operation was performed twice, and 114 g of this cis-polybutadiene was dissolved in cyclohexane, thereby preparing a cyclohexane solution of cis-polybutadiene.

[0120]

Production of vinyl-cis-polybutadiene rubber of mixture of (A) and (B) :

The foregoing cyclohexane solution of cis-polybutadiene having 114 g of cis-polybutadiene dissolved therein was charged in a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5.0 L and purged with a nitrogen gas, to which was then added the foregoing vinyl-cis-polybutadiene cyclohexane slurry containing 58 g of vinyl-cis-polybutadiene while stirring. After adding the slurry, the stirring was continued for one hour, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 172 g of a vinyl-cis-polybutadiene rubber of a mixture of (A) and

(B). This polymer mixture had an ML of 56 and an HI of 12.2 %.

[0121]

(Example 3-2)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 3-1, except for using a trade name: UBEPOL-BR150L as the cis-polybutadiene rubber manufactured by Ube Industries, Ltd. in (A). This polymer mixture had an ML of 63 and an HI of 12.0 %.

[0122]

(Example 3-3)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 3-1, except for using a product of JSR Corporation (a trade name: JSR-BR01) as the cis-polybutadiene rubber in (A). This polymer mixture had an ML of 64 and an HI of 11.7 %.

[0123]

(Example 3-4)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 3-1, except for using 30 g of a cis-polybutadiene rubber (a trade name: UBEPOL-BR130B) manufactured by Ube Industries, Ltd. and 10 g of a polyisoprene rubber (a trade name: JSR-IR2200) manufactured by JSR Corporation in (A) (BR + IR = 40 g). This polymer mixture had an ML of 58 and an HI of 12.3 %.

[0124]

(Comparative Example 3-1)

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5 L and purged with a nitrogen gas, 3.5 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 5.3 mmoles of water, 10.5 mmoles of diethylaluminum chloride, 1.8 mmoles of carbon disulfide, 40.0 mmoles of cyclooctadiene and 0.004 mmoles of cobalt octoate, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. Thereafter, 560 mL of butadiene, 4.5 mmoles of water, 13.4 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 60 °C for 20 minutes, thereby undergoing 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 350 g of a 1,4-cis-1,2-vinyl polymer. This VCR had an ML of 58 and an HI of 11.8 %.

Each of the vinyl-cis-polybutadiene rubbers of the foregoing Examples and Comparative Example was subjected to primary compounding by adding thereto and kneading therewith carbon black, a process oil, zinc white, stearic acid and an antioxidant by using a plastomill and subsequently subjected

to secondary compounding by the addition of a vulcanization accelerator and sulfur by using a roll according to a compounding table of Table 5, thereby preparing a compounded rubber. By using this compounded rubber, its die swell was measured. In addition, this compounded rubber was molded depending upon the desired physical properties and press vulcanized at 150 °C to obtain a vulcanizate, the physical properties of which were then measured. The measurement results of the respective physical properties are shown in Table 6 while taking the Comparative Example as "100".

[0125]

Table 5

	Compounding amount (parts by weight)
Vinyl-cis-polybutadiene	100
HAF carbon black	50
Process oil	10
Zinc white No. 1	5
Stearic acid	2
Antioxidant (Note 1)	1
Vulcanization accelerator (Note 2)	1
Sulfur	1.5

(Note 1) ANTAGE AS (a compound between amine and ketone)

(Note 2) NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0126]

Table 6

	3-1	3-2	Example 3-3	3-4	Comparative Example 3-1
Component (A):					
Mooney viscosity of cis-polybutadiene	29	43	44	29	-
Viscosity in toluene solution of cis-polybutadiene	30	105	150	30	-
Mooney viscosity of polyisoprene (IR) H.I. (%)	-	-	-	90	-
Component (B):	36.2	41.3	38.4	37.1	-
Mooney viscosity					
Viscosity in toluene solution	29	29	29	29	-
Whole polymer (A + B):					
Mooney viscosity	48	48	48	48	-
IR (%)					
H.I. (%)	58	63	64	58	58
12.2	12.0	11.7	12.3	11.8	-
Physical properties of compounded material:					
Die swell	95	92	94	93	100
Physical properties of vulcanizate:					
Tensile elastic modulus M100	117	120	119	118	100
Rebound resilience	102	104	103	102	100
Flexometer test:					
Heat build-up ΔT	98	96	97	97	100
Permanent set	96	95	96	95	100

[0127]

(Example 4-1)

(A) Production of vinyl-cis-polybutadiene:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 1.5 L, 40 g of a cis-polybutadiene rubber (a trade name: UBEPOL-BR150L) manufactured by Ube Industries, Ltd. and having been reprecipitated and purified was charged, and after purging with a nitrogen gas, 350 mL of cyclohexane was added for dissolution. To this solution, 150 mL of butadiene, 1.1 mmoles of water, 3.5 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing to 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto. Thereafter, the unreacted butadiene was removed by evaporation, thereby obtaining vinyl-cis-polybutadiene having an HI of 40.3 % in a yield of 67 g. 58 g of this vinyl-cis-polybutadiene was dissolved in cyclohexane to prepare vinyl-cis-polybutadiene slurry.

[0128]

(B) Production of cis-polybutadiene solution:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 3.0 L and purged with a nitrogen gas, 2.0 L of cyclohexane was charged and dissolved in 132 g of cis-cis-polybutadiene (a trade name: UBEPOL-BR150L)

manufactured by Ube Industries, Ltd. and having an ML viscosity of 43, thereby preparing a solution of cis-polybutadiene cyclohexane.

[0129]

Production of vinyl-cis-polybutadiene rubber of mixture of (A) and (B) :

The foregoing cyclohexane solution of cis-polybutadiene having 132 g of cis-polybutadiene dissolved therein was charged in a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5.0 L and purged with a nitrogen gas, to which was then added the foregoing vinyl-cis-polybutadiene cyclohexane slurry containing 58 g of vinyl-cis-polybutadiene while stirring. After adding the slurry, the stirring was continued for one hour, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 190 g of a vinyl-cis-polybutadiene rubber of a mixture of (A) and (B). This polymer mixture had an ML of 72 and an HI of 12.3 %.

[0130]

(Example 4-2)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 4-1, except for using a trade name: UBEPOL-BR130B as the cis-polybutadiene rubber manufactured by Ube Industries, Ltd. in (A). This polymer mixture had an ML of 70 and an HI of 12.0 %.

[0131]

(Example 4-3)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 4-1, except for using a product of JSR Corporation (a trade name: JSR-BR01) as the cis-polybutadiene rubber in (B). This polymer mixture had an ML of 74 and an HI of 11.9 %.

[0132]

(Example 4-4)

A vinyl-cis-polybutadiene rubber was obtained in the same manner as in Example 4-1, except for using 30 g of a cis-polybutadiene rubber (a trade name: UBEPOL-BR150L) manufactured by Ube Industries, Ltd. and 10 g of a polyisoprene rubber (a trade name: JSR-IR2200) manufactured by JSR Corporation in (A) (BR + IR = 40 g). This polymer mixture had an ML of 75 and an HI of 12.2 %.

[0133]

(Comparative Example 4-1)

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5 L and purged with a nitrogen gas, 3.5 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 5.3 mmoles of water, 10.5 mmoles of diethylaluminum chloride, 1.8 mmoles of carbon disulfide, 40.0 mmoles of cyclooctadiene and 0.004 mmoles of cobalt octoate, and the mixture was stirred at 40 °C for 20

minutes, thereby undergoing 1,4-cis-polymerization. Thereafter, 560 mL of butadiene, 4.5 mmoles of water, 13.4 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 60 °C for 20 minutes, thereby undergoing 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 350 g of a 1,4-cis-1,2-vinyl polymer. This VCR had an ML of 58.0 and an HI of 11.8 %.

[0134]

Each of the vinyl-cis-polybutadiene rubbers of the foregoing Examples and Comparative Example was subjected to primary compounding by adding thereto and kneading therewith carbon black, a process oil, zinc white, stearic acid and an antioxidant by using a plastomill and subsequently subjected to secondary compounding by the addition of a vulcanization accelerator and sulfur by using a roll according to a compounding table of Table 7, thereby preparing a compounded rubber. By using this compounded rubber, its die swell was measured. In addition, this compounded rubber was molded depending upon the desired physical properties and press vulcanized at 150 °C to obtain a vulcanizate, the physical properties of which were then measured. The measurement

results of the respective physical properties are shown in Table 8 while taking the Comparative Example as "100".

[0135]

Table 7

	Compounding amount (parts by weight)
Vinyl-cis-polybutadiene	100
HAF carbon black	50
Process oil	10
Zinc white No. 1	5
Stearic acid	2
Antioxidant (Note 1)	1
Vulcanization accelerator (Note 2)	1
Sulfur	1.5

(Note 1) ANTAGE AS (a compound between amine and ketone)

(Note 2) NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0136]

Table 8

		Example 4-1	Example 4-2	Example 4-3	Example 4-4	Comparative Example 3-1
Component (A):						
Mooney viscosity of cis-polybutadiene	29	43	44	29	-	-
Viscosity in toluene solution of cis-polybutadiene	30	105	150	30	-	-
Mooney viscosity of polyisoprene (IR)	-	-	-	90	-	-
H.I. (%)	36.2	41.3	38.4	37.1	-	-
Component (B):						
Mooney viscosity	29	29	29	29	-	-
Viscosity in toluene solution	48	48	48	48	-	-
Whole polymer (A + B):						
Mooney viscosity	56	63	64	58	58	-
IR (%)	-	-	-	5.2	-	-
H.I. (%)	12.2	12.0	11.7	12.3	11.8	-
Physical properties of compounded material:						
Die swell	95	92	94	95	100	-
Physical properties of vulcanizate:						
Tensile elastic modulus M100	117	120	119	118	100	-
Rebound resilience	102	104	103	102	100	-
Flexometer test:						
Heat build-up ΔT	98	96	97	97	100	-
Permanent set	96	95	96	95	100	-

[0137]

(Example 5)

(Rubber composition for sidewall)

(Production of vinyl-cis-polybutadiene sample 1)

(A) Production of vinyl-cis-polybutadiene:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 1.5 L and purged with a nitrogen gas, 1.0 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 1.7 mmoles of water, 2.9 mmoles of diethylaluminum chloride, 0.3 mmoles of carbon disulfide, 13.0 mmoles of cyclooctadiene and 0.005 mmoles of cobalt octoate, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. At this time, a small amount of the cis-polybutadiene polymerization solution was taken out from the reaction tank and dried, and the viscosity in a toluene solution of the resulting cis-polybutadiene rubber was measured and found to be 175. Thereafter, 150 mL of butadiene, 1.1 mmoles of water, 3.5 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing to 1,2-syndiotactic polymerization. An antioxidant ethanol solution was added thereto. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, thereby obtaining vinyl-cis-poly-

butadiene having an HI of 40.5 % in a yield of 66 g. 58 g of this vinyl-cis-polybutadiene was dissolved in cyclohexane to prepare vinyl-cis-polybutadiene slurry.

[0138]

(B) Production of cis-polybutadiene:

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 1.5 L and purged with a nitrogen gas, 1.0 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 1.7 mmoles of water, 2.9 mmoles of diethylaluminum chloride, 20.0 mmoles of cyclooctadiene and 0.005 mmoles of cobalt octoate, and the mixture was stirred at 60 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, thereby obtaining 81 g of cis-polybutadiene having a Mooney viscosity of 29.0 and a viscosity in a toluene solution of 48.3. This operation was performed twice, and 162 g in total of cis-polybutadiene was dissolved in cyclohexane, thereby preparing a cyclohexane solution of cis-polybutadiene.

[0139]

Production of vinyl-cis-polybutadiene rubber of mixture of (A) and (B):

The foregoing cyclohexane solution of cis-polybutadiene

having 162 g of cis-polybutadiene dissolved therein was charged in a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5.0 L and purged with a nitrogen gas, to which was then added the foregoing vinyl-cis-polybutadiene cyclohexane slurry containing 58 g of vinyl-cis-polybutadiene while stirring. After adding the slurry, the stirring was continued for one hour, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 220 g of a vinyl-cis-polybutadiene rubber of a mixture of (A) and (B). This polymer mixture had an ML of 61.1 and an HI of 11.9 %.

[0140]

(Production of vinyl-cis-polybutadiene sample 2)

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 5 L and purged with a nitrogen gas, 3.5 L of a polymerization solution (butadiene: 31.5 % by weight, 2-butenes: 28.8 % by weight, cyclohexane: 39.7 % by weight) was charged, to which were then added 5.3 mmoles of water, 10.5 mmoles of diethylaluminum chloride, 1.8 mmoles of carbon disulfide, 40.0 mmoles of cyclooctadiene and 0.004 mmoles of cobalt octoate, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing 1,4-cis-polymerization. Thereafter, 560 mL of butadiene, 4.5 mmoles of water, 13.4 mmoles of triethylaluminum chloride and 0.04 mmoles of cobalt octoate were added, and the mixture was stirred at 40 °C for 20 minutes, thereby undergoing 1,2-syndiotactic polymerization.

An antioxidant ethanol solution was added thereto, thereby stopping the polymerization. Thereafter, the unreacted butadiene and 2-butenes were removed by evaporation, followed by drying in vacuo at 105 °C for 60 minutes, thereby obtaining 350 g of a 1,4-cis-1,2-vinyl polymer. This VCR had an ML of 58.0 and an HI of 11.8 %.

[0141]

Physical properties of the foregoing sample 1 and sample 2 are shown in Table 9.

[0142]

Table 9

	Sample 1	Sample 2
Sample (A):		
Viscosity in toluene solution of cis-polybutadiene	175	-
H.I. (%)	40.5	-
Component (B):		
Mooney viscosity	29	-
Viscosity in toluene solution	48.3	-
Whole polymer:		
Viscosity in toluene solution of cis-polybutadiene	-	49.9
Mooney viscosity	61.1	58.8
H.I. (%)	11.9	11.8

[0143]

(Examples 5-1 to 5-5) and (Comparative Examples 5-1 to 5-3)
By using each of the foregoing sample 1 and sample 2,

compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 10 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 10.

In the table, the respective die swell, 300 % tensile elastic modulus and low fuel consumption values are relative values with respect to those in Comparative Example 5-1. Incidentally, in Comparative Example 5-1, the die swell was 2.27; the 300 % tensile elastic modulus was 9.7 MPa; and with respect to the low fuel consumption, a temperature rise of 14.7 °C was observed.

[0144]

The compositions of the Examples are greatly improved with respect to the elastic modulus and highly balanced between the die swell and the low fuel consumption as compared with those of the Comparative Examples. On the other hand, in the compositions of the Comparative Examples, when the compounding amount of carbon black is high, the exothermic characteristic

was deteriorated. Furthermore, when vinyl-cis-polybutadiene which is not satisfied in the invention is used, or the amount of use of vinyl-cis-polybutadiene of the invention is low, the improvement effects did not reached the expected levels.

[0145]

Table 10

Compounding table	Example					Comparative Example		
	5-1	5-2	5-3	Sample 1	Sample 1	Sample 1	Sample 1	Sample 1
Kind of vinyl-cis-polybutadiene Amount (parts)	60	60	60	80	40	60	60	10
NR (Note 1)	40	40	40	20	60	40	40	90
Carbon black N330	40	55	30	40	40	40	70	40
Aromatic oil	10	10	10	10	10	10	10	10
Zinc oxide	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2
Antioxidant (Note 2)	1	1	1	1	1	1	1	1
Vulcanization accelerator (Note 3)	1.0	1.0	1.0	0.9	0.8	1.0	1.0	0.7
Sulfur	1.5	1.5	1.5	1.7	2.0	1.5	1.5	2.2
Physical properties of compounded material:								
Die swell index	87	77	97	82	96	100	73	115
Physical properties of vulcanizate:								
300 % tensile elastic modulus (index)	131	162	111	113	126	100	179	80
Low fuel consumption (index)	85	93	76	80	88	100	109	103

[0146]

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ
(N-cyclohexyl-2-benzothiazole sulfenamide)

[0147]

(Examples 6-1 to 6-4) and (Comparative Examples 6-1 to 6-2)
(Silica compounded rubber composition for tire)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 11 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 11.

In the table, the respective die swell, Pico abrasion, wet skid properties and low fuel consumption values are relative values with respect to those in Comparative Example 6-1. Incidentally, in Comparative Example 6-1, the die swell was

2.69; the Pico abrasion was 156; the wet skid properties were 46; and with respect to the low fuel consumption, a temperature rise of 15 °C was observed.

[0148]

The compositions of the Examples realize a small die swell, high abrasion resistance and low fuel consumption while keeping wet skid properties as compared with those of the Comparative Examples. On the other hand, in the compositions of the Comparative Examples, in the case where vinyl-cis-polybutadiene which is not satisfied in the invention is used, or the amount of addition of silica is low, while a small die swell and high abrasion resistance are realized, a remarkable lowering of the wet skid properties is caused, whereby the desired characteristics cannot be obtained.

[0149]

Table 11

Compounding table		6-1	6-2	Example	6-3	6-4	Comparative Example
Kind of vinyl-cis-polybutadiene	Amount (parts)	Sample 1 35	Sample 1 35	Sample 1 45	Sample 1 35	Sample 2 35	Sample 1 35
NR (Note 1)	-	25	15	-	-	-	-
SRB1500	65	40	40	65	65	65	65
Carbon black N330	27	27	27	21.5	27	60	-
Silica (Note 2)	30	30	30	35	30	-	-
Silane coupling agent (Note 3)	6	6	6	7	6	-	-
Aromatic oil	15	15	15	15	15	15	15
Zinc oxide	5	5	5	5	5	5	3
Stearic acid	2	2	2	2	2	2	2
Antioxidant (Note 4)	1	1	1	1	1	1	1
Vulcanization accelerator (Note 5)	1.3	1.3	1.3	1.4	1.3	1	-
Vulcanization accelerator (Note 6)	0.7	0.7	0.7	0.9	0.7	-	-
Sulfur	2	2	2	2.1	2	2	1.8
Physical properties of compounded material:							
Die swell index	86	92	91	92	100	83	-
Physical properties of vulcanizate							
Pen abrasion (Index)	108	100	113	102	100	116	-
Wet skid properties (Index)	105	104	104	105	100	97	-
Low fuel consumption (index)	88	84	81	84	100	110	-

(Note 1) NR: RSS#1

(Note 2) BR: Polybutadiene (UBEPOL-BR150, manufacture by Ube Industries, Ltd.)

(Note 3) Ultrasil VN3 GR (manufactured by Degussa)

(Note 4) X50S (Equal-amount mixture of N330 and Si69, manufactured by Degussa)

Si69: Bis(3-triethoxysilylpropyl)-tetrasulfide

(Note 5) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 6) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

(Note 7) Vulcanization accelerator: NOCCELER D (N,N'-diphenylguanidine)

[0150]

(Examples 7-1 to 7-4) and (Comparative Examples 7-1 to 7-3)

(Rubber composition for passenger automobile tire)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 12 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and

then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 12.

In the table, the respective die swell, 300 % tensile elastic modulus, Pico abrasion and wet skid properties values are relative values with respect to those in Comparative Example 7-1. Incidentally, in Comparative Example 7-1, the die swell was 2.02; the 300 % tensile elastic modulus was 18.4 MPa; the Pico abrasion was 181; and the wet skid properties were 44.

[0151]

The compositions of the Examples realize a high elastic modulus and high abrasion resistance while keeping wet skid properties as compared with those of the Comparative Examples. On the other hand, in the compositions of the Comparative Examples, in the case where the amount of use of vinyl-cis-polybutadiene of the invention is high, vinyl-cis-polybutadiene which is not satisfied in the invention is used, or the amount of addition of SBR is low, while a high elastic modulus and high abrasion resistance are realized, a remarkable lowering of the wet skid properties is caused, whereby the desired characteristics cannot be obtained.

[0152]

Table 12

Compounding table	Example						Comparative Example 7-3
	7-1	7-2	7-3	7-4	7-1	7-2	
Kind of vinyl-cis-polybutadiene Amount (parts)	Sample 1 35	Sample 1 35	Sample 1 45	Sample 1 20	Sample 2 35	Sample 1 35	Sample 1 65
NR (Note 1)	-	25	15	40	-	55	-
SBR1500	65	40	40	40	65	10	35
Carbon black N330	60	60	60	60	60	60	60
Aromatic oil	15	15	15	15	15	15	15
Zinc oxide	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2
Antioxidant (Note 2)	1	1	1	1	1	1	1
Vulcanization accelerator (Note 3)	1.5	1.2	1.3	1.2	1.5	1.0	1.3
Sulfur	1.8	1.9	1.8	2.0	1.8	2.0	1.7
Physical properties of compounded material							
Die swell index	85	93	84	96	100	102	76
Physical properties of vulcanizate							
300 % tensile elastic modulus (index)	123	117	128	105	100	107	140
Pico abrasion (index)	108	99	112	93	100	84	116
Wet skid properties (index)	105	102	100	103	100	95	95

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0153]

(Examples 8-1 to 8-3) and (Comparative Example 8-1)

(Rubber composition for tire cord coating)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 13 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 13.

In the table, the respective die swell, 100 % green modulus, 300 % tensile elastic modulus, tensile strength and adhesive strength to metal values are relative values with respect to those in Comparative Example 8-1. Incidentally, in Comparative Example 8-1, the die swell was 2.12; the 100 % green modulus

was 0.6 MPa; the 300 % tensile elastic modulus was 18.5 MPa; the tensile strength was 28.9 MPa; and the adhesive strength to metal was 12 kg.

[0154]

The compositions of the Examples have a small die swell and largely improved green modulus while keeping a high elastic modulus and are excellent in adhesiveness to metals.

[0155]

Table 13

Compounding table	Kind of vinyl-cis-polybutadiene Amount (parts)	Example			Comparative Example 8-1
		8-1 Sample 1 35	8-2 Sample 1 20	8-3 Sample 1 35	
NR (Note 1)	65	80	65	65	65
Carbon black N330	60	60	50	50	60
Zinc oxide	7	7	7	7	7
Stearic acid	2	2	2	2	2
Cobalt stearate	3	3	3	3	3
Antioxidant (Note 2)	2	2	2	2	2
Vulcanization accelerator (Note 3)	0.8	0.8	0.8	0.8	0.8
Sulfur	1.5	1.5	1.5	1.5	1.5
Physical properties of compounded material:					
Die swell (index)	82	91	89	89	100
100 % green modulus (index)	122	110	104	104	100
Physical properties of vulcanizate:					
300 % tensile elastic modulus (index)	128	111	104	104	100
Tensile strength (index)	108	104	102	102	100
Adhesive strength to metal (index)	110	108	106	106	100

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0156]

(Examples 9-1 to 9-5) and (Comparative Examples 9-1 to 9-4)

(Rubber composition for base stread)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 14 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 14.

In the table, the respective die swell, 100 % green modulus, 300 % tensile elastic modulus and exothermic characteristic values are relative values with respect to those in Comparative Example 9-1. Incidentally, in Comparative Example 9-1, the die swell was 2.25; the 300 % tensile elastic modulus was 10.1 MPa;

and with respect to the exothermic characteristic, a temperature rise of 16.5 °C was observed.

[0157]

The compositions of the Examples are greatly improved with respect to the elastic modulus and highly balanced between the die swell and the exothermic characteristic. On the other hand, in the compositions of the Comparative Examples, when the compounding amount of carbon black is high, the exothermic characteristic is deteriorated. Furthermore, when the compounding amount of carbon black is low, the die swell and the elastic modulus are largely deteriorated. Furthermore, when the amount of use of vinyl-cis-polybutadiene of the invention is low, the improvement effects did not reached the expected levels.

[0158]

Table 14

Compounding table	Example						Comparative Example				
	9-1	9-2	9-3	9-4	Sample 1	9-5	Sample 1	Sample 2	9-2	9-3	9-4
Kind of vinyl-cis-polybutadiene Amount (parts)	Sample 1 50	Sample 1 70	Sample 1 30	Sample 1 50	Sample 1 50	Sample 1 50	Sample 1 50	Sample 1 50	Sample 1 50	Sample 1 50	Sample 1 10
NR (Note 1)	50	30	70	50	50	50	50	50	50	50	90
Carbon black N330	40	40	40	50	35	40	40	60	20	40	
Aromatic oil	10	10	10	10	10	10	10	10	10	10	
Zinc oxide	5	5	5	5	5	5	5	5	5	5	
Stearic acid	2	2	2	2	2	2	2	2	2	2	
Antioxidant (Note 2)	1	1	1	1	1	1	1	1	1	1	
Vulcanization accelerator (Note 3)	1.0	0.9	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.7
Sulfur	1.5	1.7	2.0	1.5	1.5	1.5	1.5	1.5	1.5	1.5	2.2
Physical properties of compounded material:											
Die swell index											
Physical properties of vulcanizate:											
300 % tensile elastic modulus (index)	137	149	106	147	120	100	157	80	82		
Exothermic characteristic (index)	84	80	89	96	77	100	112	90	100		

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0159]

(Examples 10-1 to 10-5) and (Comparative Example 10-1)

(High-hardness compounded rubber composition)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 15 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 15.

In the table, the respective die swell, hardness and low exothermic characteristics values are relative values with respect to those in Comparative Example 10-1. Incidentally, in Comparative Example 10-1, the die swell was 1.50; the hardness was 78; with respect to the low exothermic

characteristics, a temperature rise of 45 °C was observed.

[0160]

The compositions of the Examples have largely improved die swell and exothermic characteristics while keeping a high hardness.

[0161]

Table 15

	Compounding table	Example						Comparative Example 10-1 Sample 2 50
		10-1 Sample 1 50	10-2 Sample 1 70	10-3 Sample 1 30	10-4 Sample 1 50	10-5 Sample 1 50		
Kind of vinyl-cis-polybutadiene	Amount (parts)							
NP (Note 1)	50	30	70	50	50	50	50	50
Carbon black N330	70	70	70	60	80	70		
Aromatic oil	5	5	5	10	10	10	5	
Zinc oxide	5	5	5	3	3	3	5	
Stearic acid	2	2	2	2	2	2	2	
Antidioxidant (Note 2)	1	1	1	1	1	1	1	
Vulcanization accelerator (Note 3)	1.0	1.2	0.8	1.0	1.0	1.0	1.0	
Sulfur	3.0	2.8	3.2	3.0	3.0	3.0	3.0	
Physical properties of compounded material:								
Die swell index	84	76	96	93	73	73	100	
Physical properties of vulcanizate:								
Hardness (index)	106	113	103	103	108	100	100	
Low exothermic characteristics (index)	87	80	92	78	91	100		

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

[0162]

(Examples 11-1 to 11-3) and (Comparative Example 11-1)

(Rubber composition for large-sized vehicle tire)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 16 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a rubber composition for sidewall. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 16.

In the table, the respective die swell, 300 % tensile elastic modulus, Pico abrasion and wet skid properties values are relative values with respect to those in Comparative Example 11-1. Incidentally, in Comparative Example 11-1, the die swell was 1.81; the 300 % tensile elastic modulus was 16.3

MPa; the Pico abrasion was 226; and the wet skid properties were 40.

[0163]

The compositions of the Examples have a small die swell and have excellent wet skid properties and abrasion resistance while keeping a high elastic modulus as compared with that of the Comparative Example. On the other hand, in the composition of the Comparative Example, since vinyl-cis-polybutadiene which is not satisfied in the invention is used, the abrasion resistance is not enhanced, or the wet skid properties are lowered, whereby the desired characteristics cannot be obtained.

[0164]

Table 16

Compounding table		11-1	11-2	11-3	Comparative Example
	Amount (parts)	Sample 1 30	Sample 1 20	Sample 1 30	Sample 2 30
NR (Note 1)	70	80	70	70	70
Carbon black N330	60	60	50	50	60
Aromatic oil	10	10	10	10	10
Zinc oxide	3	3	3	3	3
Stearic acid	2	2	2	2	2
Antioxidant (Note 2)	1	1	1	1	1
Vulcanization accelerator (Note 3)	0.8	0.8	0.8	0.8	0.8
Sulfur	1	1	1	1	1
Physical properties of compounded material:					
Die swell (Index)	84	91	90	90	100
Physical properties of vulcanizate:					
300 % tensile elastic modulus (index)	125	111	106	106	100
Pico abrasion (index)	113	105	101	101	100
Wet skid properties (index)	105	108	107	107	100

(Note 1) NR: RSS#1

(Note 2) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 3) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

Industrial Applicability

[0165]

According to the invention, as compared with the conventional vinyl-cis-polybutadiene rubber, vinyl-cis-polybutadiene having satisfactory processability and having excellent exothermic characteristics and rebound resilience can be produced. When the vinyl-cis-polybutadiene obtained by the invention is used for tire application, in the production step, the workability of tire manufacture is enhanced due to its excellent extrusion processability so that it becomes possible to realize low fuel consumption of the completed tire.

Also, according to the invention, it is possible to provide a rubber composition for sidewall having low fuel consumption with respect to a vulcanizate thereof and having a small die swell.

Also, according to the invention, it is possible to provide a silica compounded rubber composition for tire having excellent extrusion processability and having satisfactory wet skid properties and abrasion resistance while keeping a high elastic modulus.

Also, according to the invention, it is possible to provide a tire for passenger automobile having excellent extrusion molding processability and having satisfactory high-speed running properties, grip properties on a wet road surface and abrasion resistance by using a rubber composition for cap tread having excellent extrusion processability while keeping a high elastic modulus.

Also, according to the invention, it is possible to provide a rubber composition for tire cord coating of carcasses, belts, beads, etc. having a small die swell, a large green strength and excellent molding processability and having a large elastic modulus with respect to a vulcanizate thereof.

Also, according to the invention, it is possible to provide a rubber composition for base tread having low exothermic characteristics with respect to a vulcanizate thereof and having a small die swell.

Also, according to the invention, it is possible to provide a rubber composition capable of improving dimensional stability at the time of extrusion processing and durability with respect to a tire thereof while keeping a high hardness.

Also, according to the invention, it is possible to provide a rubber composition for large-sized vehicle having excellent moldability and having satisfactory high-speed running properties, wet skid properties and abrasion resistance by using a rubber composition for cap tread having

a small die swell and excellent extrusion processability while keeping a high elastic modulus.